

OFFICE OF NAVAL RESEARCH

Grant: N00014-95-WR-20027

PR Number: 96PRO-3804

Technical Report No. 14

COMPLEX IMPEDANCE MEASUREMENTS ON NAFION

by

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Prepared for Publication in
Electrochimica Acta

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19961016 137

DTIC QUALITY INSPECTED 4

September 19, 1996

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	September 19, 1996	Technical Report 6/1/96 - 5/31/97
4. TITLE AND SUBTITLE Complex Impedance Measurements on NAFION		5. FUNDING NUMBERS Grant: N00014-95-WR-20027 PR Number: 96PRO-3804 Robert J. Nowak
6. AUTHOR(S) Mary C. Wintersgill and John J. Fontanella		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) United States Naval Academy Physics Department Annapolis, MD 21402		8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report #14
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Chemistry Division 800 North Quincy Street Arlington, VA 22217-5660		10. SPONSORING/MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES Prepared for Publication in <u>Electrochimica Acta</u>		
12a. DISTRIBUTION / AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.		12b. DISTRIBUTION CODE
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14. SUBJECT TERMS nafion, complex impedance, electrical conductivity, high pressure, activation volume, methanol.		15. NUMBER OF PAGES 16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED
		20. LIMITATION OF ABSTRACT

COMPLEX IMPEDANCE MEASUREMENTS ON NAFION

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Abstract--The need to develop an electrolytic membrane for an efficient, environmentally sound fuel cell has lead to intense interest in proton conducting polymers in general and Nafion in particular. While it does not appear very likely that Nafion itself will ultimately prove to be the best choice of material, it may be considered as a prototype membrane material. Initial interest focused on Nafion's potential use in a hydrogen fuel cell, in which case its conductivity in the presence of water is important and so extensive studies of the electrical properties of Nafion at various levels of humidity were carried out. Two distinct regimes were identified, one at lower water contents and the other at high water contents. The possible conduction mechanisms associated with these regimes will be discussed. In addition, studies carried out at high pressure yielded activation volumes which provide further clues as to the conduction mechanisms involved. More recently, interest in Nafion as a membrane material in methanol fuel cells has prompted investigation of its electrical properties in the presence of methanol alone and of methanol/water mixtures. It is clear that not only is Nafion an excellent proton conductor, but it also exhibits significant methanol transport. This represents a serious crossover problem for fuel cell applications and it is important to be able to characterize the mechanisms involved.

Key words: nafion, complex impedance, electrical conductivity, high pressure, activation volume, methanol.

INTRODUCTION

The continuing initiatives to develop viable fuel cells for a wide range of applications have stimulated interest in membrane materials such as Nafion, which is a perfluorosulfonic ionomer developed by DuPont de Nemours Co. The primary interest originally arose from the high proton conductivity observed in these materials, but it quickly became apparent that Nafion was highly permeable to a number of different molecules. Early measurements revealed that the proton conductivity was strongly associated with water content and studies have been undertaken by several groups [1-17]. That work has shown that Nafion exhibits a range of electrical phenomena. In addition, there is a large number of representations which have been used to present the data, particularly when complex impedance measurements have been carried out. For the most part, the results from different groups are consistent. However, in some cases there is disagreement in the interpretation of the results. Those circumstances will also be discussed and new data are presented which reflect on at least one of the controversies. Finally, the results of complex impedance studies at high pressures and variable water and methanol concentrations will be discussed.

ELECTRICAL PHENOMENA

Dielectric Relaxation in "Dry" Nafion

Complex impedance measurements on Nafion samples which have been dried thoroughly by heating in a vacuum at 380K for about 2 weeks reveal two distinct types of electrical phenomena below about 400K. First, "true" dielectric relaxation is observed. What is meant by "true" dielectric relaxation is the reorientation of electrical dipoles where the centers are fixed in position. Since the term dielectric is synonymous with insulator, this can only be observed when Nafion is an insulator and, in fact, dry Nafion is a good insulator at low temperatures. Such measurements are often displayed in terms of the real and imaginary parts of the complex dielectric constant, $\epsilon^* = \epsilon' - j\epsilon''$, which are determined as follows. The bridge most frequently used by the authors measures the equivalent parallel capacitance (C) and resistance (R) of the sample. These quantities are convenient for dielectric relaxation measurements since the real and imaginary parts of the dielectric constant for a parallel plate capacitor geometry are calculated from:

$$\epsilon' = Cd/\epsilon_0 A \quad (1)$$

and

$$\epsilon'' = \epsilon' G/\omega C \quad (2)$$

where d is the thickness (length) of the sample, A is the area of the sample and ϵ_0 is the permittivity of free space. It is also traditional to display dielectric relaxation data in terms of $\tan \delta$, which is given by:

$$\tan \delta = \epsilon''/\epsilon' \quad (3)$$

This has the advantage of being independent of geometry but has disadvantages concerning the interpretation of the peak position in cases where dipole reorientation is being studied. For a Debye relaxation, for example, while ϵ'' reaches a maximum at $\omega\tau=1$, $\tan\delta$ does not [20,21]. However, the $\tan\delta$ representation is useful for comparing relaxations in two different materials.

For example, figure 1 shows $\tan\delta$ for dry Nafion 117 and 120 and Membrane C, respectively, in the vicinity of 200K. The results are to be compared with the ϵ'' data given in Ref. 17 for Nafion 117. The low temperature relaxation in Nafion 120 is essentially identical to the γ relaxation in Nafion 117. On the other hand, the peak in Membrane C is shifted to a lower frequency, 300 vs. 1000 Hz. In addition, the peak is much stronger in Membrane C. Chemically, the only difference between Membrane C and the Nafions is the equivalent weight since Membrane C has an equivalent weight of 900 while Nafion 117 and 120 have equivalent weights of 1100 and 1200, respectively. The data shown in figure 1 indicate that it is more difficult for the average dipole to reorient in Membrane C and that there is a larger number of dipoles for Membrane C. Both effects may be due to an increased fraction of amorphous phase in Membrane C since it is generally accepted that γ relaxations are associated with the amorphous phase [22,23]. It will be of interest to extend the work to Nafion 105, which has an equivalent weight of 1000, which is intermediate between Membrane C and Nafion 117.

The low temperature peak in these fluoropolymers is consistent with the γ relaxations in related materials like PTFE, FEP and PFA [24,25] and the shift in the location of the peak with frequency as temperature changes is that expected for a normal relaxation. A best fit to the peak position versus $1000/T$ data for Nafion 117 by an Arrhenius expression yields an activation enthalpy of about $E = 0.57$ eV. The enthalpy for the γ relaxation for Nafion 120 is the same and that for Membrane C will be slightly higher.

Electrical Conductivity in "Dry" Nafion

At higher temperatures, peaks in ϵ'' vs. frequency are not observed even though large values of ϵ'' are obtained. In fact, plots of ϵ'' vs. frequency exhibit a $1/\omega$ dependence similar to that shown in Figure 2 for the "long" sample. (Figure 2 actually displays the results for a wet sample which will be discussed in the next section.) This behavior is indicative of a region of frequency independent electrical conductivity since it is obvious from equations (1) and (2) that the electrical conductivity, σ , is related to the ϵ'' via:

$$\sigma = \epsilon_0 \epsilon'' \omega \quad (4)$$

This is attributed to ionic conductivity of the material. It is interesting that even in Nafion which is nominally dry, there is still significant ion mobility, which, of course is part of the reason for the interest in Nafion as a fuel cell membrane material. It would appear, in fact, that it is extremely difficult to remove all traces of water from the material. However, it is not clear that the electrical conductivity observed in "dry" Nafion at elevated temperatures is due to water. It may be attributable to residual ions or trace impurities. Whatever the source, the ionic conductivity is relatively low. However, when water is intentionally added to the system, conductivities can be comparatively very high. This high ionic mobility presents a challenge in analyzing complex impedance data in a meaningful manner.

Blocking Electrode Effects

When the electrical conductivity is high, either because of the addition of water to Nafion or presumably for dry Nafion at very high temperatures, it is possible for a significant number of ions to reach the electrodes before the reversal

of polarity of the applied field. This results in charge build up at the electrodes when the charge carriers are not able to cross from the electrolyte into the electrodes. This is sometimes known as the blocking electrode or space charge or interfacial effect. Of course, the electrodes can be partially blocking and, depending upon the nature of the charge carriers and the electrodes themselves, these effects lead to a myriad of phenomena. Two fairly common characteristics of blocking electrode effects are anomalously large values of ϵ' and low values of ϵ'' and hence σ . Another characteristic is also apparent. In recent papers, Fontanella et al. [4] and Cahan and Wainright [11] have pointed out that the frequency dependent electrical conductivity

$$\sigma = \sigma_0 \omega^n \quad (5)$$

which has been frequently reported for Nafion [5] is actually due to blocking electrode and space charge effects and does not represent a characteristic of the bulk electrical conductivity.

Another phenomenon appears in figure 9 of a paper by Su and Mauritz [16] where the imaginary part of the admittance, Y'' , is plotted. A peak is observed and attributed to "H₂O Dipole Rotation" despite the fact the frequency of the peaks is on the order of MHz while water dipole rotation is usually on the order of GHz. The effect that sample configuration can have on such measurements is illustrated by some complex impedance measurements which were carried out two different lengths of acid form Nafion 117 conditioned over distilled water (100% relative humidity). The measurements were made along the plane of the film at frequencies from about 100 Hz to 10 MHz at room temperature and atmospheric pressure. Each film had approximately the same width and the short sample was approximately 1

mm long while the long sample as about 20 mm long. The results are shown in Figures. 2-4. It is apparent from Figure 2 that a straight line with a slope close to -1 is observed for the $\log_{10}(\epsilon'')$ vs. $\log_{10}(f(\text{Hz}))$ plot for the long sample. The conductivity, itself, is shown in Figure 3 and is seen to be relatively constant. It is also apparent from Figs. 2 and 3 that for the short sample, the values of ϵ'' and σ are anomalously low as would be expected for blocking electrode or space charge effects as was discussed previously. Of most importance, however, is the plot of Y'' vs. $\log_{10}(f(\text{Hz}))$ given in Figure 4. It is clear that the short sample, which is dominated by blocking electrode or space charge effects, exhibits a peak while the long sample does not. Consequently, a peak in Y'' vs $\log_{10}(f(\text{Hz}))$ plot is not necessarily characteristic of a microscopic property of the material such as dipole rotation and thus care must be taken in interpreting Y'' data.

Electrical Conductivity in "Wet" Nafion

The most commonly used representation of electrical data for materials with high ionic conductivity is complex impedance, $Z^* = 1/Y^* = Z' - jZ''$. Often, a complex impedance diagram, Z'' versus Z' , is plotted because it is usually straightforward to separate bulk from interface effects. An example of such a plot for Nafion 120 conditioned at 25% and 45% relative humidity is shown in Figure 5. Frequencies increase from right to left. It is seen that this material exhibits the standard depressed, semicircular arc at the higher frequencies which is associated with the bulk properties of the material. At low frequencies a slanted line is observed which is associated with blocking electrodes or space charge. The bulk resistance of the sample is taken to be the value of Z' at the intersection of the two regions.

The frequency range over which either the arc or the straight line segment will be observed depends strongly on the conductivity of the material and the sample configuration and observation of these features provides a crucial check that

bulk properties are indeed being measured. Results obtained from manipulation of complex impedance measurements made in regimes in which space charge effects dominate frequently exhibit interesting frequency dependences, but these results are very sensitive to the nature of the electrodes and the interface so that it is difficult to extract useful information from them.

Data on the bulk conductivity of Nafion, on the other hand, exhibit reproducible and informative results. For example, the dependence of the electrical conductivity on the amount of water present in the material can be determined as is shown in Figure 5. The shift in the intercept of the arc from high to low resistance as the water content increases is clear. This type of data has been used to obtain bulk conductivities for several different types of Nafion with a range of water contents [13,15]. The electrical conductivity data have been replotted in Figure 6 in terms of λ , the number of waters per sulfonate. This plot makes it obvious that the electrical conductivity is higher for the lower equivalent weight material when plotted vs. λ . This reflects the fact that there is more water per unit volume for the lower molecular weight material at a given λ . It has also been shown [13,15] that the electrical conductivity is approximately the same for all molecular weights for a given wt.-%. One final feature of interest is that electrical conductivity in Nafion is often interpreted in terms of percolation [26]. It will be of interest to determine how percolation relates to the electrical conductivity data shown in Figure 6.

Electrical Conductivity at High Pressure

Another way in which complex impedance has been used to learn about electrical conductivity in Nafion is to carry out the experiments under high pressure. It is sometimes useful to interpret the pressure dependence of the conductivity in terms of an activation volume, which can be thought of as the

dilatation of the material associated with the conduction mechanism. The activation volume is given by:

$$\Delta V = -kT [\partial \ln \sigma / \partial p]_T. \quad (5)$$

The room temperature activation volumes from ref. 15 are plotted vs. water content in Figure 7. The activation volumes for various dilutions of sulfuric acid as calculated from complex impedance analysis are also included for comparison. As can be seen in Figure 7, ΔV exhibits two different types of behavior.

At low water content, $\lambda < 5$, the activation volume is positive since the electrical conductivity decreases as pressure increases. This is the case for both Nafion and sulfuric acid, but the value is much smaller for sulfuric acid. The interpretation is that in both cases the viscosity is the dominant factor since in general it is expected that viscosity should increase with pressure. In the case of Nafion, the viscosity is probably attributable to the polymer via segmental motions, presumably those of the pendant chains, hence the relatively large value of activation volume. For concentrated sulfuric acid, on the other hand, the small, positive activation volume is attributed to dominance of "normal" liquid viscosity and thus the smaller activation volume is not surprising.

At high water concentration (large λ) the activation volume has similar negative values for both Nafion and sulfuric acid since the ionic conductivity increases as pressure increases. This suggests similarity between ionic conductivity in high water content Nafion and dilute sulfuric [15]. There are some significant differences, however. The increase in conductivity with pressure for dilute sulfuric acid is usually attributed to "increasing ionization of the bisulfate ion with increasing pressure. The increased ionization is presumably due to enhanced hydration of the ions caused by increasing pressure [27-29]." The difficulty in

directly comparing Nafion with sulfuric acid, of course, is that the bisulfate ion, HSO_4^- , does not exist in Nafion. However, it is interesting that a similar entity, HSO_3^- , does exist in Nafion though it is bonded to the polymer. Further, the ionization of HSO_3^- is responsible for most of the free protons in Nafion. However, it is generally thought that HSO_3^- is completely ionized in wet Nafion. Consequently, further ionization with the increase of pressure should be impossible and thus should not be responsible for an increase in electrical conductivity with high pressure. As pointed out in reference 15, most of the increase of electrical conductivity with pressure can probably be accounted for by the compressibility which merely reflects the fact that because the volume decreases as pressure increases, the charge carrier concentration and hence the electrical conductivity will increase. However, that argument was made approximating the compressibility of high water content Nafion by the value for water and assuming the the viscosity (or mobility of the ions) does not change with pressure. Since neither quantity is known and since both are necessary for a proper evaluation of the effect of pressure on the electrical conductivity, further work concerning this point is necessary.

Electrical Conductivity in Nafion Containing Methanol and Water

The investigation of the electrical conductivity of Nafion in the presence of methanol and water has recently begun. Some preliminary results are being presented at this conference [30]. The interesting result is that different behavior is observed for methanol/water mixtures at low and high solution concentrations. At low solution content the electrical conductivity is higher than would be expected based on the electrical conductivity of the individual constituents while the reverse is true at high water content. Again, this is explained in terms of different behavior of Nafion at low and high values of λ . At low solution content, where segmental motions are important, the electrical conductivity is anomalously high because of

plasticization i.e. the segmental motions are enhanced because of the presence of the methanol. At high values of λ , where the electrical conductivity is dominated by the solution, the electrical conductivity is lower because of the presence of the methanol i.e. the electrical conductivity is lower in methanol.

SUMMARY

In summary, then, some aspects of complex impedance studies of Nafion have been discussed. Three distinct types of phenomena are often observed, dielectric relaxation, electrical conductivity and blocking electrode effects. It is shown how dielectric relaxation gives information concerning polymer structure. It is also shown that particular care must be taken when blocking electrode effects are important. That occurs when samples are very thin/short or are very conductive. Next, it is shown how the results of complex impedance studies of Nafion at various concentrations of water and high pressure can be used to gain insight into electrical conductivity in Nafion. Finally, the results of studies of methanol and methanol-water mixtures in Nafion are discussed.

Acknowledgments--This work was supported in part by the Office of Naval Research.

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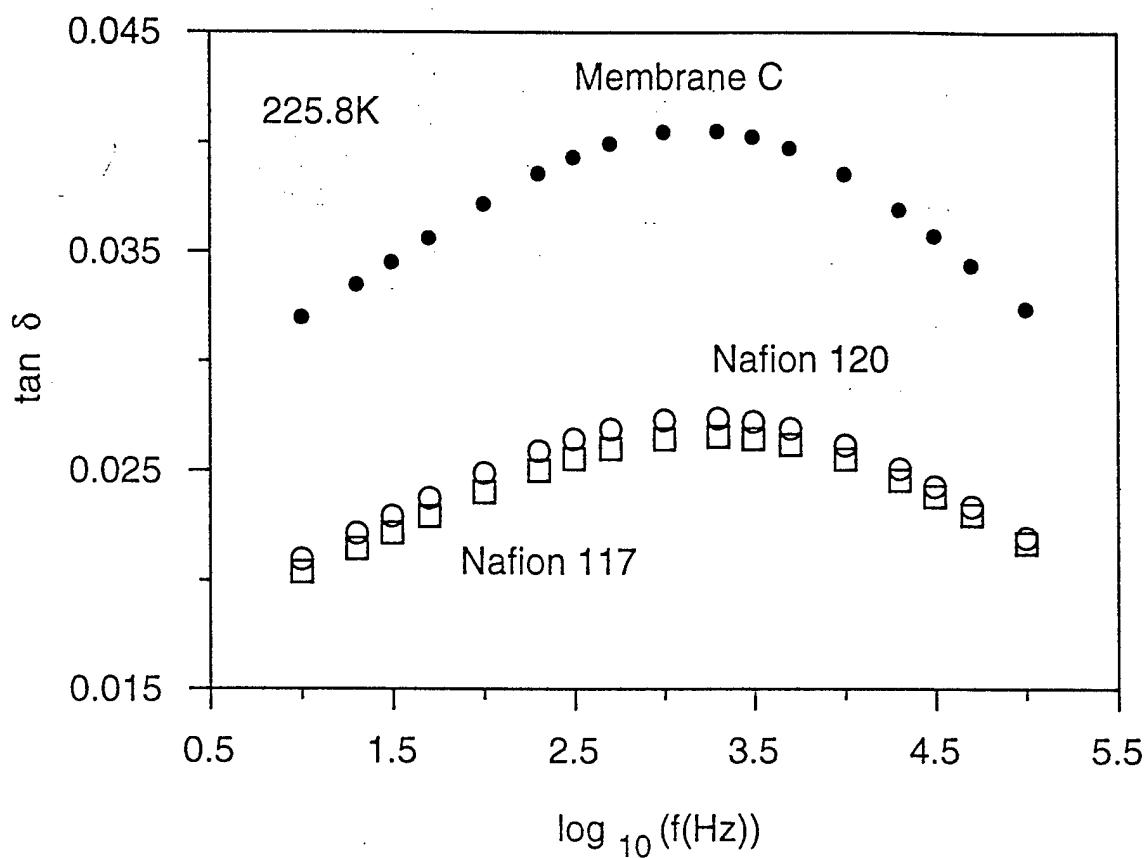


Figure 1. Dielectric loss vs. the logarithm of the frequency for Nafion 120 at two different water contents and room temperature (about 298 K). The closed symbols are for Membrane C, the open circles are Nafion 120 and the squares are Nafion 117.

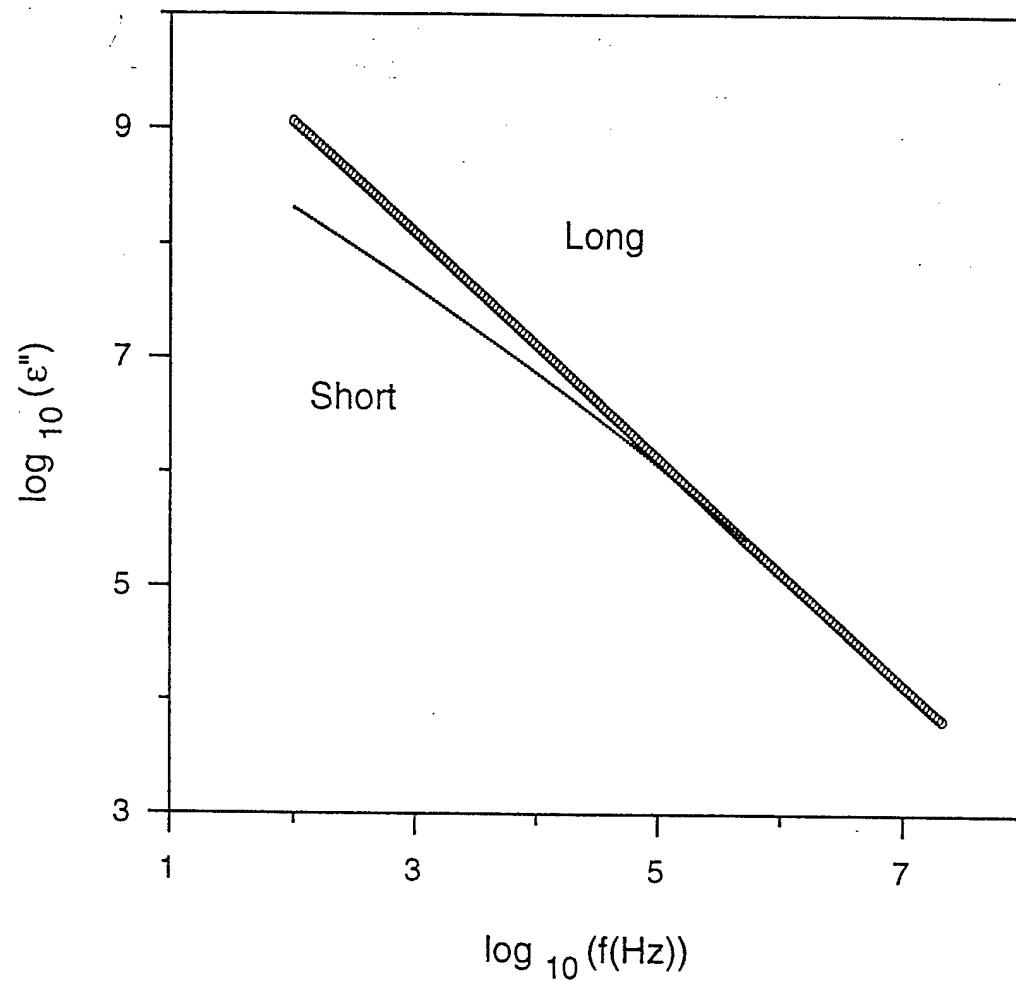


Figure 2. Logarithm of the imaginary part of the dielectric constant, ϵ'' , vs. the logarithm of the frequency for Nafion 117. The "short" sample was approximately 1 mm long while the "long" sample was about 2 cm long.

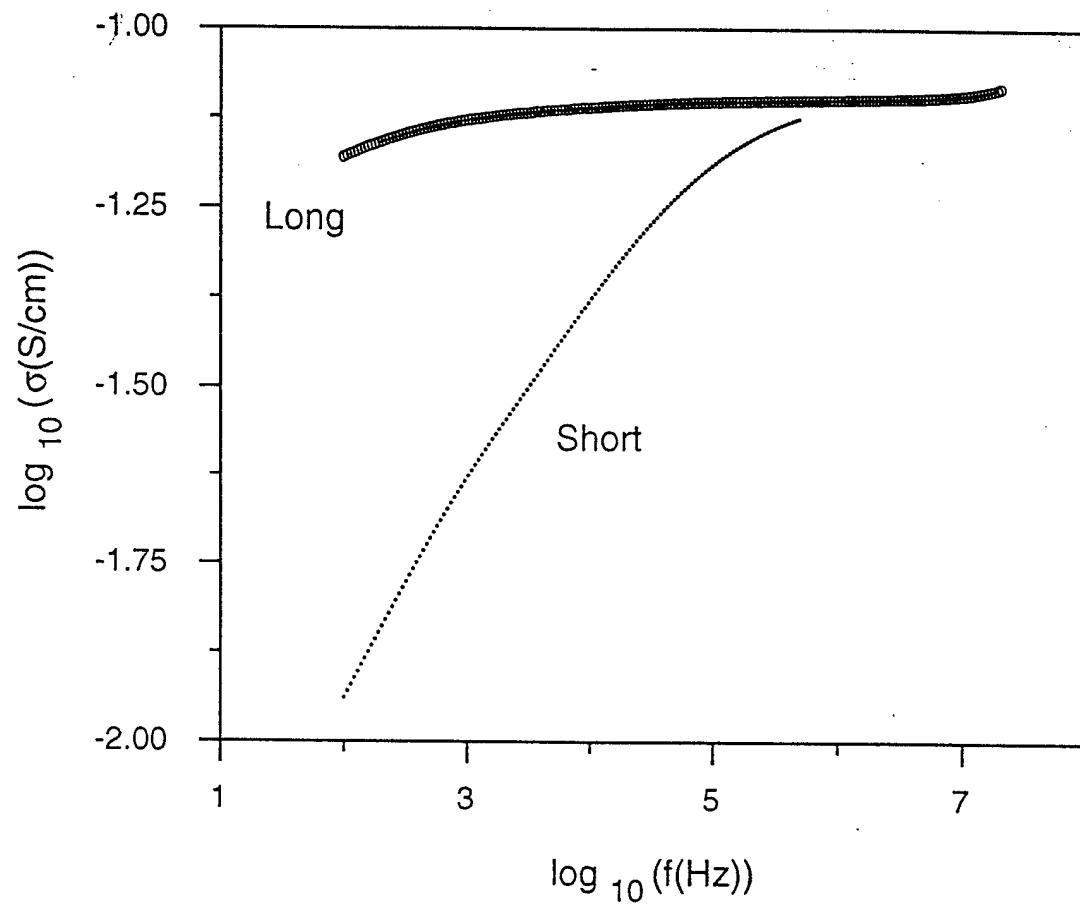


Figure 3. Logarithm of the apparent electrical conductivity, σ , vs. the logarithm of the frequency for Nafion 117. The "short" sample was approximately 1 mm long while the "long" sample was about 2 cm long.

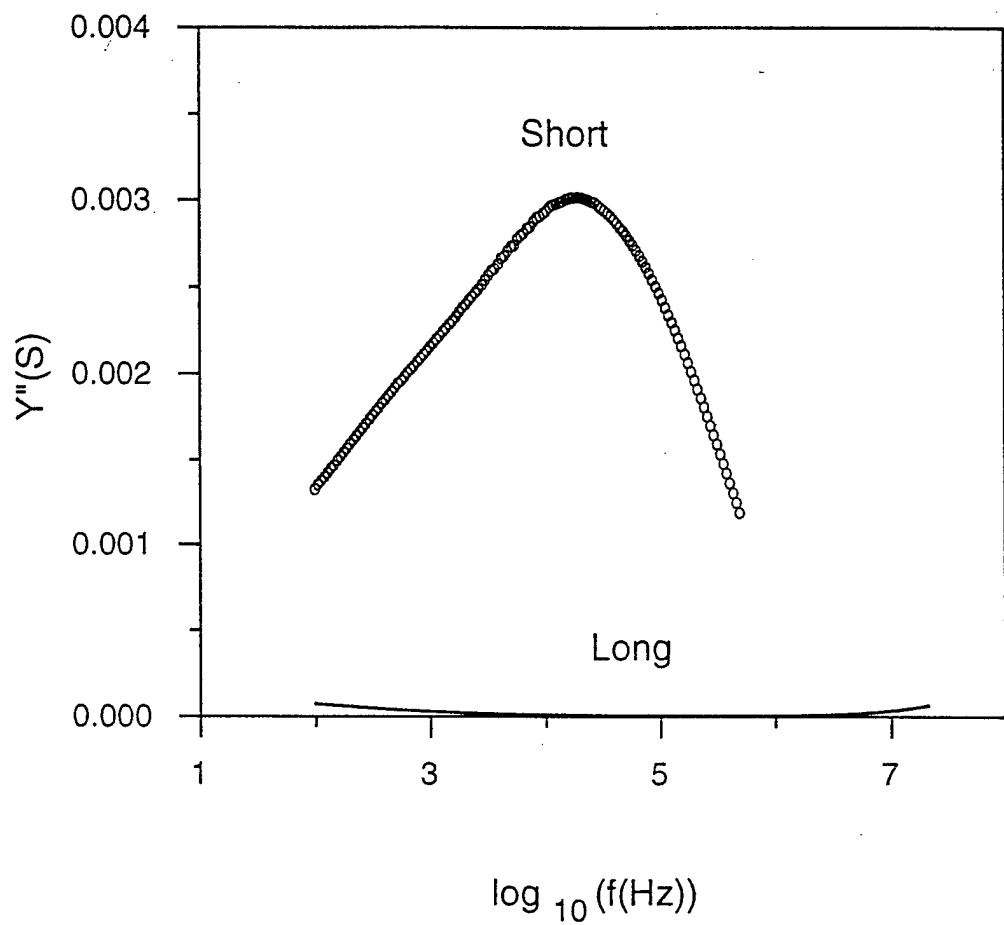


Figure 4. Imaginary part of the complex admittance, vs. the logarithm of the frequency for Nafion 117. The "short" sample was approximately 1 mm long while the "long" sample was about 2 cm long.

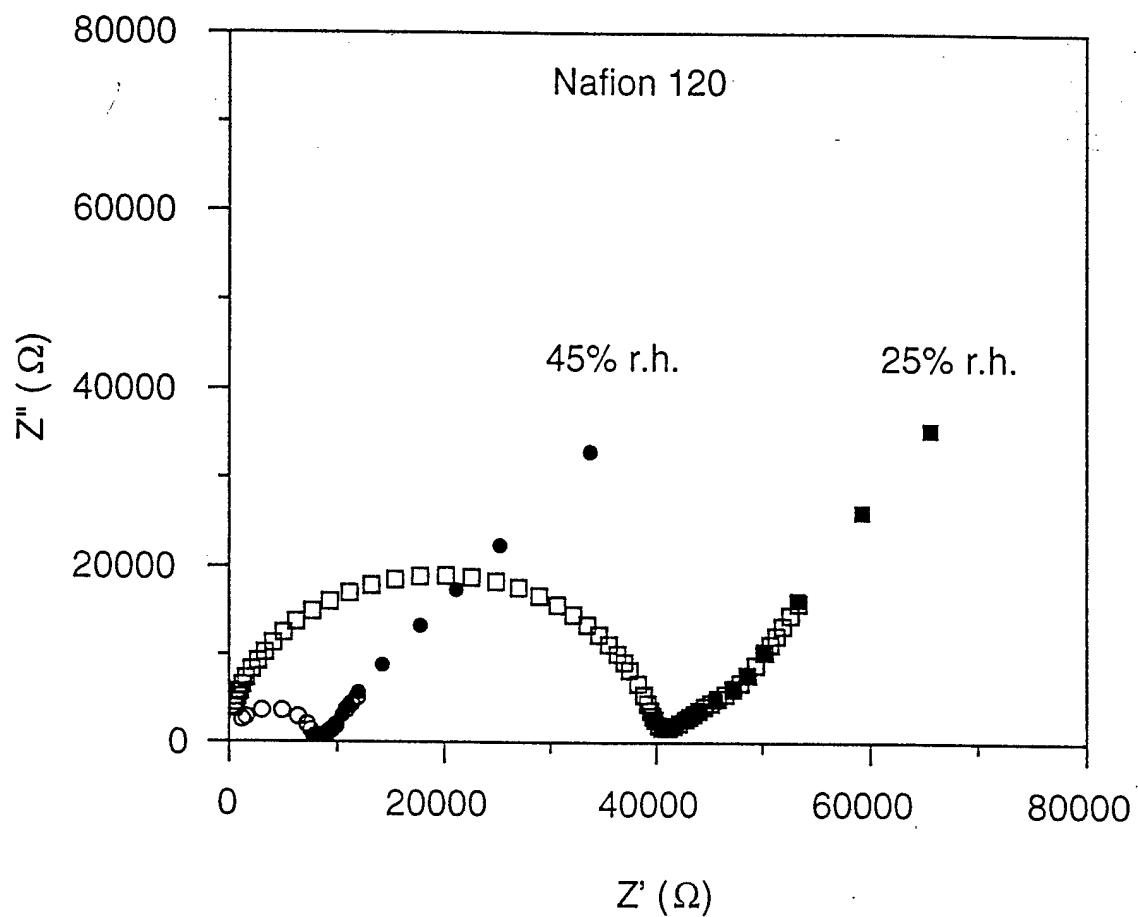


Figure 5. Complex impedance plots for Nafion 120 treated at two different relative humidities, 25% and 45%. The solid symbols were determined using a CGA-83 Capacitance Measuring Assembly and the open symbols were measured using a HP 4194 Impedance Gain/Phase Analyzer.

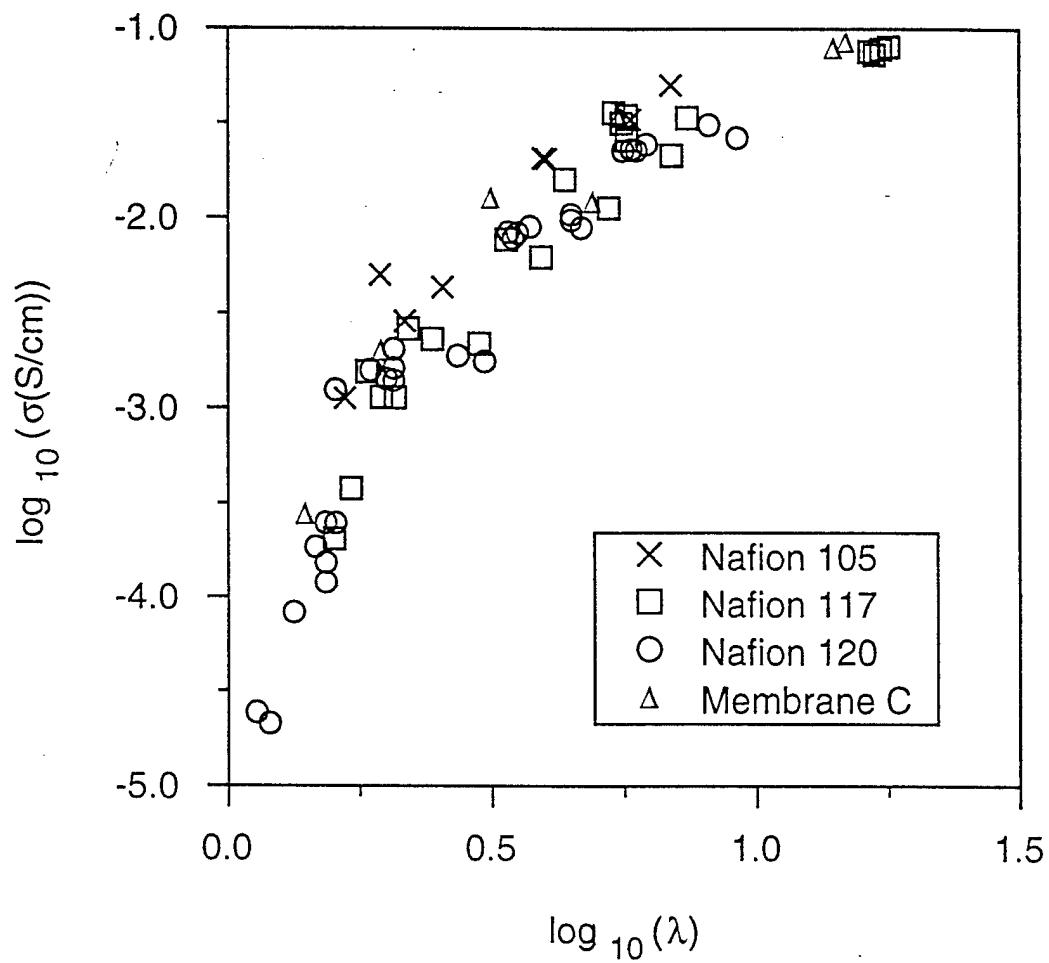


Figure 6. Logarithmic plot of the electrical conductivity vs. water content for various samples of Membrane C and Nafion 105, 117 and 120 at room temperature (about 298 K). The data are from refs. 13 and 15.

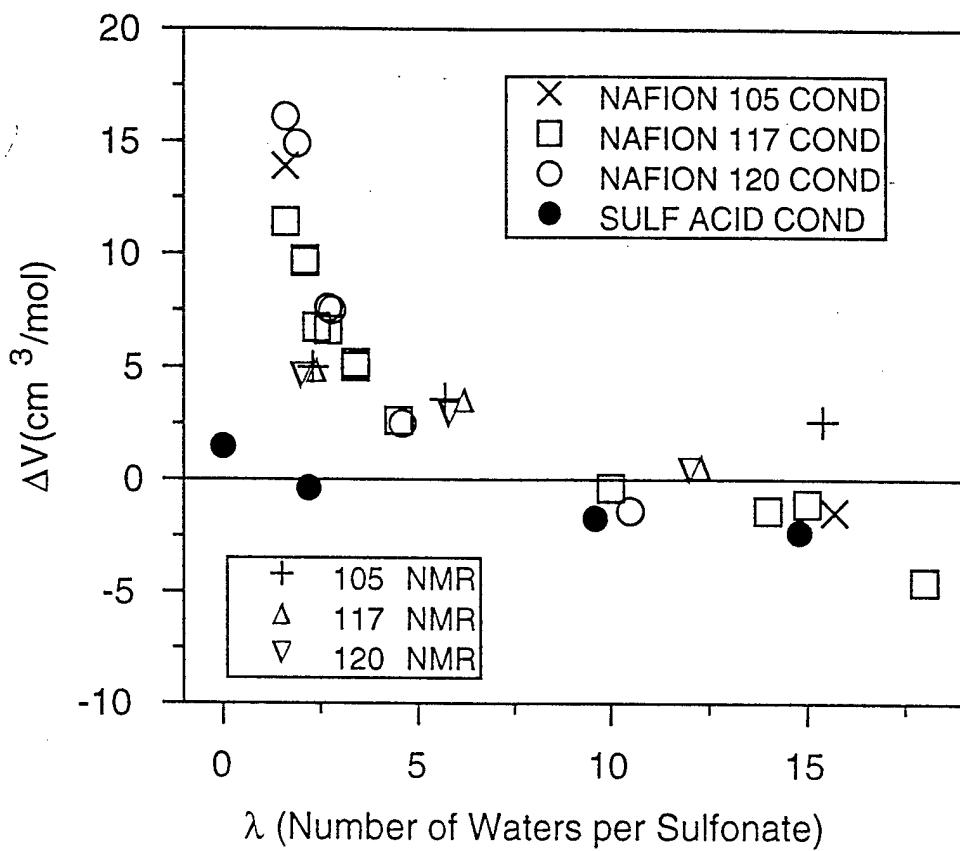


Figure 7. Activation volume vs. water content for sulfuric acid and various samples of Nafion 105, 117 and 120 at room temperature (about 298 K). All data are from ref. 15.